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## (54) PROCESS FOR THE MANUFACTURE OF ENZYME-CONTAINING GRANULES

(71) We, KNAPSACK AKTIENGESELLSCHAFT, a body corporate organised under the Laws of Germany, of 5033 Knapsack bei Köln, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is an improvement in or modification of the process described in Patent Specification No. 1217639 and enables granules which have a good storage life and contain minor proportions of dusty constituents to be obtained.

Patent Specification No. 1217639 describes and claims a process for the manufacture of enzyme-containing granules suitable for use as detergent or cleansing agent components, the granules substantially consisting of a hydrated alkali metal or ammonium salt of an inorganic or organic acid and minor proportions of an enzyme and a cellulose ether, which process comprises spraying an aqueous solution or suspension of a cellulose ether and an enzyme onto a hydratable, anhydrous or partially hydrated alkali metal or ammonium salt of an inorganic or organic acid, wherein the cation of the salt used is the lithium, sodium, potassium or ammonium ion, and its acid component consists of sulfuric acid, a polyphosphoric acid, nitrilotriacetic acid or ethylene diaminetetracetic acid, and, while effecting the spraying step, granulating the whole with thorough agitation.

The polyphosphoric acid salts include more particularly sodium tripolyphosphate, sodium pyrophosphate or sodium hexametaphosphate. Sodium tripolyphosphate with a phase-I content of at most about 80 weight percent is particularly preferred as an anhydrous or partially hydrated representative of these compounds. Alkali metal or ammonium salts hydrated to an extent of about 3%, for example, may be mentioned as partially hydrated starting materials useful for granulation.

A further feature of this process comprises using as the enzymes hydrolases, such as proteases, esterases, carbohydrases and nucleases or oxidoreductases, transferases, desmolases or isomerases. The enzymes may be used in the form of pure, dry powder or in the form of blends, for example with sodium sulfate, which are sometimes commercially available. The hydrolases and more particularly the proteases are of particular interest amongst the enzyme groups specified above. The proteases catalyze the hydrolysis of the peptide-linkages of proteins, polypeptides and similar compounds with the resultant formation of free amino and carboxylic groups, and thus cause break-up of protein-structured contaminants, during the washing step. Protease representatives suitable for use in the process include pepsin, trypsin, chymotrypsin, collagenase, keratinase, elastase, papain, carboxypeptidase, aminopeptidase, and serinproteases.

A further preferred feature of the process described in Patent Specification No. 1217639 comprises making the granules with the use of a cellulose ether binder.

The starting materials suitable for granulation may be used, for example, in the following proportions:

hydratable, anhydrous or partially hydrated alkali metal or ammonium salt: about 50 to 90 weight percent

pure enzyme dry substance: about 0.1 to 10 weight percent

cellulose ether: about 0.01 to 4 weight percent.

The alkali metal or ammonium salt is preferably sprayed using an aqueous solution or suspension which contains between about 0.1

and 10 weight percent of a cellulose ether and between about 0.1 and 25 weight percent enzyme dry substance. It is also possible to use an aqueous cellulose ether solution or suspension with a quantity of water therein which is sufficient to effect partial or complete hydration of the alkali metal or ammonium salt in the finished granules. For example, the aqueous cellulose ether solution may contain a proportion of water sufficient to effect hydration of between 5 and 98%, preferably between 93 and 98%, and more preferably of about 96%, of the alkali metal or ammonium salt present in the finished granules. It is also possible, if necessary or convenient, to use the aqueous cellulose ether solution in excess with respect to the quantity of water needed to effect complete hydration of the alkali metal or ammonium salt. In this event, it is necessary for the granules to be freed from the water in excess, for example by evaporation during the granulating step.

During the granulation of the alkali metal or ammonium salt or its hydration, which occurs simultaneously, the blend is heated to temperatures which may affect the enzyme and hence reduce its activity. To avoid this, it is advantageous to take steps which effectively prevent the mixture from exceeding temperatures of about 70°C, for example, by cooling it.

The granules are more particularly produced in the following manner:

The anhydrous or partially hydrated alkali metal or ammonium salt is placed, for example, in a turbulent air mixer, on a rotary plate or in a mixing drum, agitated therein, and a predetermined quantity of an aqueous solution or suspension with a definite concentration of cellulose ether and enzyme therein is simultaneously sprayed onto the said alkali metal or ammonium salt, if desired while cooling.

It has now unexpectedly been discovered that the granules described in Patent Specification No. 1217639, can also be produced by using a binder other than a cellulose ether binder, without affecting the properties of the resulting granules.

The process of the present invention, therefore, being an improvement in the process claimed in Patent Specification No. 1217639 for the manufacture of enzyme-containing granules suitable for use as detergent or cleansing agent components, which substantially consist of a hydrated alkali metal or ammonium salt of an inorganic or organic acid and minor proportions of an enzyme and a cellulose ether, by spraying an aqueous solution or suspension of a cellulose ether and an enzyme onto a hydratable, anhydrous or partially hydrated alkali metal or ammonium salt of an inorganic or organic acid, wherein the cation of the salt used is the lithium, sodium, potassium or ammonium ion and the acid component consists of sulfuric acid, a polyphosphoric acid, nitrilotriacetic acid, or ethylene diamine tetracetic acid, and, while effecting the spraying step, granulating the whole with thorough agitation, comprises more particularly replacing the cellulose ether by at least one binder selected from the group consisting of dextrin, alginate, agar-agar, gum arabic, tragacanth, polyvinyl alcohol, bassorin and guar gum.

Between about 50 and 90 weight percent of hydratable, anhydrous or partially hydrated alkali metal or ammonium salt, between about 0.1 and 10 weight percent of pure enzyme dry substance, and between about 0.01 and 4 weight percent of binder are used in carrying out the granulation in accordance with the present invention. The aqueous solution or suspension sprayed onto the said alkali metal or ammonium salt contains between about 0.1 and 10 weight percent of binder and between about 0.1 and 10 weight percent of binder and between about 0.1 and 25 weight percent of enzyme dry substance.

The invention also includes enzyme-containing detergent or cleansing agent components produced by the process defined in the last preceding paragraph but one containing at least one binder selected from the group consisting of dextrin, alginate, agar-agar, gum arabic, tragacanth, bassorin and guar gum.

As builder substances, the granules may contain any of the above-mentioned alkali metal or ammonium salts of which the cation is a lithium, sodium, potassium or ammonium ion, and the acid component consists of sulfuric acid, a polyphosphoric acid, nitrilotriacetic acid or ethylene diaminetetracetic acid. Preferably, however, the detergent or cleansing agent components contain hydrated sodium tripolyphosphate, sodium pyrophosphate or sodium hexametaphosphate as the said salt. The detergent or cleansing agent components also contain enzymes, such as hydrolases, oxidoreductases, transferases, desmolases or isomerases; the hydrolases include more particularly proteases, esterases, carbohydrases or nucleases. The pure enzyme is used in a proportion of between about 0.1 and 10 weight percent and the binder is used in a proportion of between about 0.01 and 4 weight percent, based on the weight of the detergent or cleansing agent component.

The granules of the present invention are more particularly produced in the following manner:

The anhydrous or partially hydrated alkali metal or ammonium salt is placed, for example, in a turbulent air mixer, on a rotary plate or in a mixing drum, agitated therein, and a predetermined quantity of an aqueous solution or suspension having a definite concentration of binder and enzyme therein is simultaneously sprayed onto the said alkali metal or ammonium salt, if desired while cooling. Very coarse, particulate granules are obtained in this

manner. This is very desirable for use thereof in detergent or cleansing agents. The individual granulate particles have the good stability which is so desirable, and contain granulated enzyme whose activity is only immaterially reduced, during the granulating step. In addition thereto, the finished granules are immediately ready for use as a detergent component without the need to subject it to a postripening step. The use of binders in the present invention finally adds to improving the detergents' capacity for suspending dirt.

It has been an unexpected discovery that the use of an aqueous solution or suspension of a suitable binder in combination with an enzyme as a granulation auxiliary entails the advantageous effects described above, bearing in mind that it has not been possible heretofore in analogous cases to produce granules having a quality comparable with that of the present products, with the use of non-ionic, surface-active substances as the granulation auxiliaries.

The following Examples and the Table hereinafter show that the present invention is a very desirable step forward in the are as discussed hereinabove.

Example 1:

69.6 Parts by weight of anhydrous, readily flowable sodium tripolyphosphate were placed in a turbulent air mixer and granulated therein by spraying a suspension of 10 parts by weight of bacterial protease, 19.2 parts by weight of water and 1.0 part by weight of dextrin thereonto. The bacterial protease had an activity of 130 000 Löhlein/Volhard-units. The resulting granules had a good flowability and the individual granular particles a good stability.

Example 2:

The procedure was the same as that described in Example 1, save that 1.0 part by weight of gum arabic was substituted for the dextrin. The flowability of the granules and the stability of the individual granular particles were good.

Example 3:

The procedure was the same as that described in Example 1, save that 0.1 part by weight of pure sodium alginate having a viscosity of between 2000 and 3000 centipoises, determined in a 2% solution at 20°C as described by Höppler, was substituted for the dextrin. The resulting granules had a good flowability and the individual granular particles a good stability.

Example 4:

The procedure was the same as that described in Example 1, save that 0.5 part by weight of polyvinyl alcohol, dissolved in ethanol, was substituted for the dextrin. The ethanolic solution had a viscosity of between 500 and 1000 centipoises, determined in a 2% solution at 20°C as described by Höppler. The resulting granules had a good flowability and the individual granular particles a good stability.

The particle size distribution in the granules produced in Examples 1 to 4 was determined by analysis. The results indicated in the following Table were obtained:

TABLE

| Granules of Example No. | Particle size distribution (%) | | | |
|---|---|---|---|---|
| | >0.84 mm | >0.5 mm | >0.2 mm | <0.2 mm |
| 1 | 32 | 78 | 93 | 7 |
| 2 | 39 | 73 | 93 | 7 |
| 3 | 36 | 69 | 95 | 5 |
| 4 | 41 | 77 | 95 | 5 |

As can be seen from the Table, the various granules contain a relatively large proportion of granular particles with maximum particle size and a small proportion of granular particles with minimum particle size. This is very desirable for the preparation of detergents.

WHAT WE CLAIM IS:—

1. Improvement in the process claimed in Patent Specification No. 1217639 for the manufacture of enzyme-containing granules suitable for use as detergent or cleansing agent components, which substantially consist of a hydrated alkali metal or ammonium salt of an inorganic or organic acid and minor proportions of an enzyme and a cellulose ether, by spraying an aqueous solution or suspension of a cellulose ether and an enzyme onto a hydratable, anhydrous or partially hydrated alkali metal or ammo-

nium salt of an inorganic or organic acid, wherein the cation of the salt used is the lithium, sodium, potassium or ammonium ion and the acid component consists of sulfuric acid, a polyphosphoric acid, nitrilotriacetic acid, or ethylene diamine tetracetic acid, and, while effecting the spraying step, granulating the whole with thorough agitation, the improvement comprising replacing the cellulose ether by at least one binder selected from the group consisting of dextrin, alginate, agar-agar, gum arabic, tragacanth, polyvinyl alcohol, bassorin and guar gum.

2. A process as claimed in claim 1, wherein the material to undergo granulation is composed of between about 50 and 90 weight percent of a hydratable, anhydrous or partially hydrated alkali metal or ammonium salt, between about 0.1 and 10 weight percent of pure enzyme dry substance, and between about 0.01 and 4 weight percent of binder.

3. A process as claimed in claim 1 or 2, wherein the alkali metal or ammonium salt is sprayed with an aqueous solution or suspension containing between about 0.1 and 10 weight percent of a binder and between about 0.1 and 25 weight percent of enzyme dry substance.

4. Enzyme-containing detergent or cleansing agent components prepared by a process as claimed in any one of claims 1 to 3, containing at least one binder selected from the group consisting of dextrin, alginate, agar-agar, gum arabic, tragacanth, bassorin and guar gum.

5. Detergent or cleansing agent components as claimed in claim 4, wherein the said alkali metal or ammonium salt is a salt of which the cation is a lithium, sodium, potassium or ammonium ion, and the acid component consists of sulfuric acid, a polyphosphoric acid, nitrilotriacetic acid or ethylene diaminetetracetic acid.

6. Detergent or cleansing agent components as claimed in claim 4 or 5, wherein the said salt is hydrated sodium tripolyphosphate, sodium pyrophosphate or sodium hexametaphosphate.

7. Detergent or cleansing agent components as claimed in any one of claims 4 to 6, wherein the enzyme is a hydrolase, oxidoreductase, transferase, desmolase or isomerase.

8. Detergent or cleansing agent components as claimed in claim 7, wherein the hydrolase is a protease, esterase, carbohydrase or nuclease.

9. Detergent or cleansing agent components as claimed in any one of claims 4 to 8, containing the pure enzyme in a proportion of between about 0.1 and 10 weight percent.

10. Detergent or cleansing agent components as claimed in any one of claims 4 to 9, containing between about 0.01 and 4 weight percent of binder.

11. A process for the manufacture of enzyme-containing granules for use as a detergent or cleansing agent component conducted substantially as described in any one of Examples 1 to 4 herein.

12. Enzyme-containing detergent or cleansing agent components whenever obtained by a process as claimed in any one of claims 1 to 3 and 11.

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